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Trend Analysis Reveals a Recent Reduction in Mirex Concentrations in Coho (*Oncorhynchus kisutch*) and Chinook (*O. tshawytscha*) Salmon from Lake Ontario

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Lake Ontario, bordering both Canada and the United States, is the only Great Lake with persistent, significant levels of mirex in its biota. Some models suggested that it would take hundreds of years before mirex disappeared from the ecosystem. From 1977 to 1996 the mirex concentrations in coho and chinook salmon greater than 2 kg in weight exceeded the 0.1 mg/kg Food and Drug Administration (FDA) action level for mirex. To determine temporal trends in salmonine mirex levels, slopes and elevations of the regression lines of mirex concentration versus fish weight were compared for each of the six sampling years (1977, 1982, 1986, 1992, 1996, and 1999) by ANCOVA with weight as a covariate. Within 24 years of mirex being banned, mirex least-squares mean concentrations in salmon fillets had decreased significantly. ANCOVA revealed that the slope of the 1999 regression line was significantly flatter ($P \leq 0.014$) than the slopes of all other regression lines except 1996 ($P = 0.966$). A Tukey test revealed that the elevation of the 1999 regression line was also significantly lower than all other years ($P < 0.001$). Based on our results, mirex concentrations in the fillets of most salmon under the size of 12 kg are now below the 0.1 mg/kg United States FDA action level for human consumption. Models suggest that mirex reductions in biota are most likely due to the settling of mirex-contaminated organisms to the sediments and the loss of mirex from the lake through the St. Lawrence River. A third mechanism is suggested as the cause of the higher rate of reduction observed in the mid to late 1990s—the control and removal of contaminated groundwater at the former Hooker Chemical site on the Niagara River, the major source of mirex in the watershed of Lake Ontario.

Introduction

Many multifunctional or "wonder" chemicals were manufactured and distributed in the 1960s. Ultimately, some of them were proven to be carcinogenic and toxic. Mirex (dodecachloropentacyclo[5.3.0.0.^{2,6}0.^{3,9}0^{4,8}]decane) is one of these multifunctional chemicals that was used as a pesticide to control fire ants in the southern United States and also as a fire-retardant in the manufacturing of plastics (*1*−*3*). This organochlorine insecticide is a major contaminant of Lake Ontario sediments and biota (*1*, *3*−*5*).

Lake Ontario, bordering both Canada and the United States, is the only Great Lake with persistent, significant levels of mirex in its biota (*1*). Hooker Chemical and Plastics Corporation manufactured mirex from 1959 through 1976. Hooker Chemical (now Occidental Chemical Corporation) on the Niagara River and Armstrong Cork Company on the Oswego River are responsible for the release of and subsequent contamination of the lake with mirex (*1*−*4*). Mirex was first discovered in Lake Ontario fish in 1974 and was found throughout the food web (*6*). In 1976, the Canadian Ontario Ministry of the Environment and the Ministry of Natural Resources concluded that all fish species tested from Lake Ontario contained mirex; however, the salmonines were the only species that exceeded the 0.1 mg/kg United States Food and Drug Administration (FDA) guideline for human consumption (*1*). Subsequently, the use of mirex as a pesticide was banned in Canada in 1977 and in the United States in 1978 (*1*, *3*).

Estimates suggest that during a 40-year period, 2700 kg of mirex entered the Lake Ontario ecosystem, of which only 550 kg have been removed by transport to the St. Lawrence estuary (*7*). Like most organochlorine compounds, mirex is generally unreactive, breaking down photochemically, with the primary photolytic product being 8-monohydro mirex, or photomirex (*8*−*10*), which is also unreactive and toxic (*11*, *12*). Mirex is not readily metabolized by most organisms (*13*−*15*) and biomagnifies in the food web, increasing in concentration with each step in the food chain (*16*). This is a concern to Lake Ontario anglers, as the salmonines are inedible according to the 0.1 mg/kg FDA action limit for mirex. Importantly, the New York Department of Health (*17*) advisory for chinook salmon in Lake Ontario is "eat none".

In 1996, an estimated 188 210 anglers fished for a total of 2.5 million days in Lake Ontario (*18*) generating over $170 000 000 dollars through sport fishing trips to New York's Great Lakes waters (*18*−*20*). Despite the consumption advisories, there is evidence (*21*, *22*) that mirex is entering into the human food chain. For example, women who ate salmon from Lake Ontario had increased levels of mirex and photomirex in their breast milk compared to women who ate panfish (i.e. perch, sunfish, and bass) or who did not eat any fish from Lake Ontario (*22*). Also, mirex levels in lactating women geographically near Lake Ontario are slightly higher, but not significantly higher, than those of women further away from the lake (*21*). Health officials, sport fishing enthusiasts, and fishery managers are interested in the residence time of mirex in Lake Ontario and more importantly how long will the salmonines remain contaminated.

Published information on temporal trends in contaminant levels of mirex in fish from Lake Ontario since the mid 1970s is meager (*5*). Often trend analysis of lipophilic contaminant levels in fish has been based solely on average concentrations. Trend analysis is limited in determining historical trends due to the confounding effects that fish age has on weight and lipid content and therefore contaminant concentrations (*23*). A more effective analysis of temporal trends is to evaluate concentrations of the contaminants as a function of weight for each year of the trend analysis. Historical trends in contaminants can then be determined by evaluating the slope and elevation of a regression line of concentration versus

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TABLE 1. Instrumentation, Chromatographic Columns, and Quality Control Procedures Employed[a]

	GC	column	mass spectrometer confirmation (% difference)	GC, spike (% recovery)	GC, sample replication (% RSD)
1977	HP5750B	4′ × 1/8″ glass packed w/3.8% UCW-982 on 80/100 Chromosorb WHP	none	91	
1982	HP5750B	4′ × 1/8″ glass packed w/3.8% UCW-982 on 80/100 Chromosorb WHP	HP5970-A MS crossed-linked DMS fused silica cap column (12.5 m × 0.2 mm i.d.) (used for qualitative confirmation)	90	19
1986	HP5750B	1.8 m × 2 mm glass packed w/3.8% UCW-982 on 80/100 Chromosorb WHP	none	113	23
1992	HP5890 w/ HP3396A Integrator	Supelco PTE-5 fused silica capillary column (30 m × 0.25 mm × 25 μm i.d.)	HP5890 series II GC w/ HP5970B MS J&W DB-5 wide bore column (15 m with 0.25 μm coating) (0% difference)	119	20
1996	HP5890 w/ HP3396A Integrator	Supelco PTE-5 fused silica capillary column (30 m × 0.25 mm × 25 μm i.d.)	HP5890 series II GC w/ HP5970B MS J&W DB-5 wide bore column (15 m with 0.25 μm coating) (12.8% difference, $P = 0.363$ *t*-test)	105	3.2
1999	HP5890 w/ HP3396 Integrator	Agilent Technology HP-5 fused silica capillary column (30 m × 0.25 mm × 25 μm i.d.)	G1800C GCD plus HP-5MS cross-linked PH ME siloxane (30 m × 0.25 mm × 25 μm i.d.) (6.7% difference, $P = 0.826$ *t*-test)	116	16.3

[a] % RSD is the percent relative standard deviation between replicates and the % difference is the percent difference between the gas chromatograph and mass spectrometer analytical results for the same sample extracts.

weight using analysis of covariance (ANCOVA) with weight as the covariate. Using this procedure, we analyzed the temporal trends in mirex concentrations in coho and chinook salmon *(Oncorhynchus kisutch* and *O. tschawytscha*, respectively). We report here on a 22-year data set that demonstrated a recent significant decrease in mirex levels in fillets of Lake Ontario salmon. Currently, mirex concentrations in the fillets of most salmon under the size of 12 kg are below the 0.1 mg/kg United States FDA guideline for human consumption.

Methods

Sample Collection. As part of a long-term study, chinook (*Oncorhynchus tshawytscha*) and coho salmon (*Oncorhynchus kisutch*) were collected during their spawning run of fall 1977, 1982, 1986, 1992, 1996, and 1999. An equal number of coho and chinook salmon were collected for analysis in 1977, 1982, and 1986. In 1992 and 1996, Coho represented 42% of the fish analyzed, while in 1999 Coho represented 32% of the fish analyzed. All salmonids were collected by electroshocking at Sandy Creek, Hamlin, NY, a tributary on the south shore of Lake Ontario (Figure 1). Fish length and weight, sex, and age (scales) were determined by standard procedures (*24*). For chemical analysis, a standard fillet consisting of the entire side of the fish from just behind the operculum to the tail, including the skin, bones of half the rib cage, and one pelvic fin but excluding the vertebrae, dorsal, pectoral, anal and caudal fins (*5, 25*), was taken, homogenized using a food processor, and stored in solvent rinsed glass jars at 0 °C.

Mirex Analysis. All 22 years of mirex analyses followed Makarewicz et al. (*26*), as revised from Insalaco et al. (*23*). In general, 5 g of homogenized fish sample was mixed with 20 g of anhydrous sodium sulfate. The samples were extracted overnight (16 ± 2 h) in Soxhletic extractors (a minimum of 200 cycles) with 75 mL of methylene chloride/hexane (20:80 v/v) solvent mixture. A 15 mL aliquot was concentrated to 1 mL under nitrogen gas and then cleaned up through a 5 g florisil column (at a rate of 4 mL/min) to a volume of 50 mL. This eluant was then concentrated under nitrogen gas to a final volume of 1 mL.

In 1977, 1982, and 1986 packed columns were employed and a nitration procedure (*27, 23*) was necessary for removing interfering PCBs. After 1986, nitration was unnecessary as capillary gas chromatography columns were employed. Prior to cleanup, percent extractable lipid content was determined by evaporating a known volume of the extract and weighing the residue (*28*).

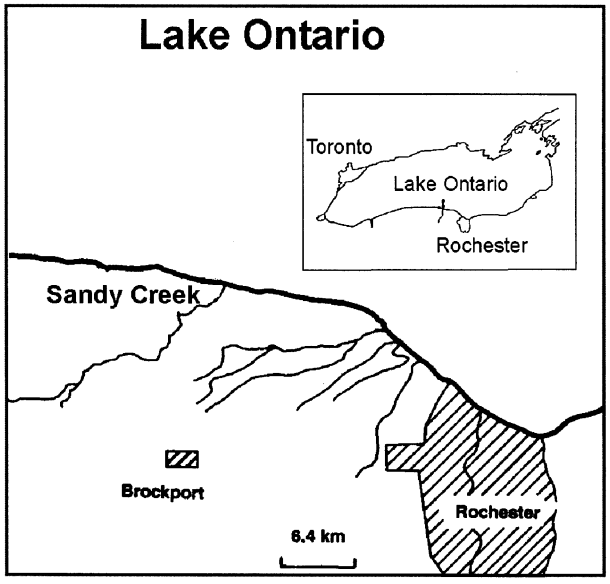

FIGURE 1. Location of the sampling site at Sandy Creek, NY, a tributary of Lake Ontario.

Quantitation of mirex and photomirex was by electron capture (^{63}Ni) gas chromatography. Confirmation of mirex and photomirex presence was by GC/MS (Table 1). Quality control procedures included analysis of extraction blanks, replicates, spike recovery efficiencies, interyear crossover studies, and cross-laboratory studies. Analysis of the same fish tissue (chinook #4, 1977) by the six different analysts over the 22-year period revealed no significant difference ($P > 0.05$, Student's *t*-test) in mirex residues. In conjunction with the New York State Department of Environmental Conservation, a cross-lab study with the State University of New York at Brockport revealed an insignificant difference ($P > 0.05$, Student's *t*-test) in mirex residues analyzed from the same fish. These interyear and interlaboratory crossover studies demonstrated a consistency in quantitation over time

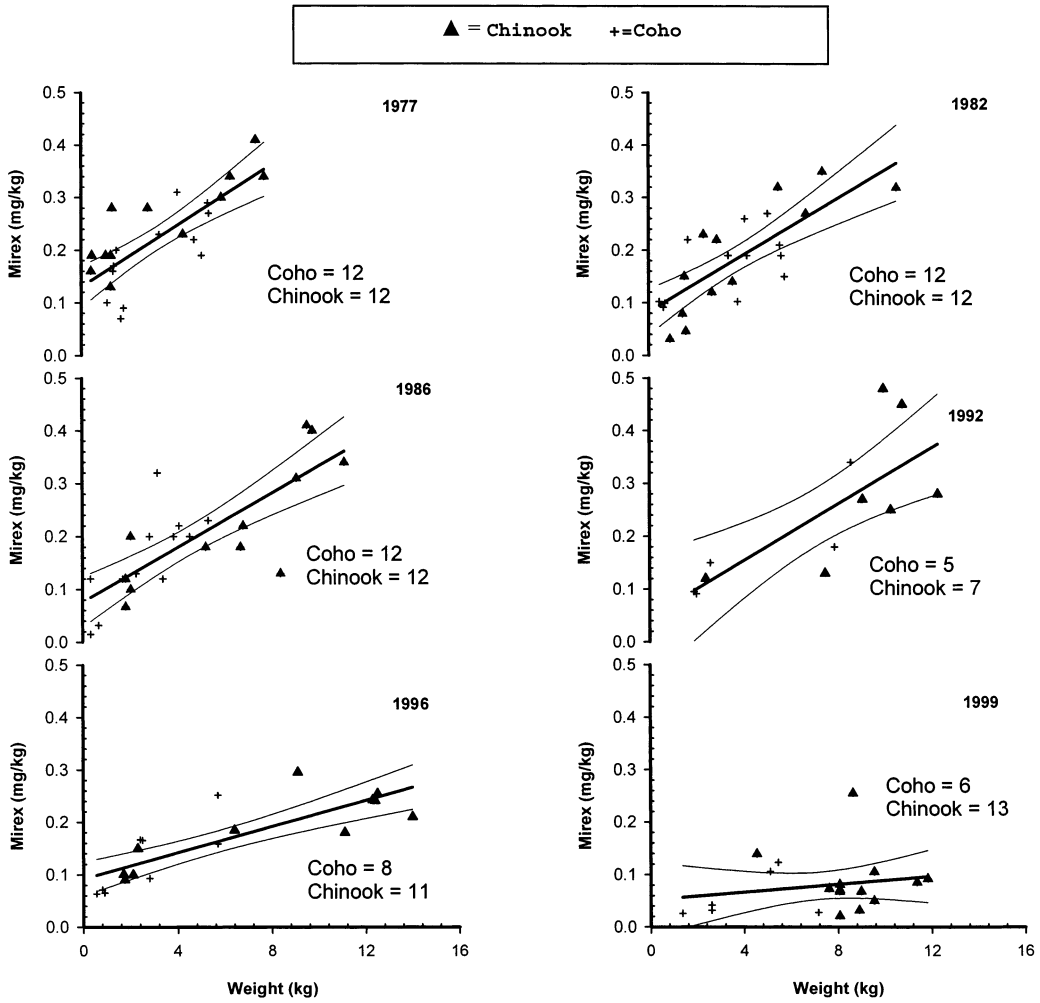

FIGURE 2. Mirex concentration versus weight of Coho or Chinook salmon for each year of the study. Shown are the simple regression lines in the scatter plot with the 95% confidence interval. Coho = 12 represents the number of fish sampled.

and between analytical laboratories. Table 1 lists the different instruments, columns, and recovery efficiencies for each year of analysis.

Statistical Analysis. Since mirex concentrations in coho and chinook salmon fillets were not significantly different ($p > 0.05$, Students's *t*-test (*23*), species data were combined for statistical analysis. Visual inspection of species-specific data (Figure 2) also support the pooling of the Chinook and Coho data. Temporal trends in mirex concentrations in fish fillets were statistically compared by two different methods using SPSS 10.0.5 (SPSS Inc.): Analysis of Variance (ANOVA) was used to test for temporal trends in average annual mirex concentrations of salmonines independent of weight, and Analysis of Covariance (ANCOVA) was used to test for temporal trends in mirex concentrations with salmonine weight as the covariate and weight × sampling year as the interaction term. A significant interaction term indicated that the slope of the mirex concentration-salmon weight regression line was dependent on the sampling year. Slopes of each regression line were compared using a pairwise *t*-test of all possible pairs, in which the significance levels were corrected using Bonferroni layering (*29*). Regression line elevations were also analyzed for significant differences using a Tukey HSD test of the least-squares means (LSMEANS) for each sampling year. The LSMEANS are the means for the salmon mirex concentration after they have been adjusted for the covariate of weight.

Results

Significant differences (ANOVA, $F = 7.32$, df = 5,115, $P < 0.001$) were observed in mirex concentrations in salmon over the 22-year period (Table 2). Tukey HSD tests revealed that average mirex concentrations in salmon collected in 1999 were lower ($P < 0.05$) than in all other years of collection (Table 2). No other consistent temporal trend was obvious. Average mirex concentration decreased from 0.22 to 0.19 mg/kg in the 1977 to 1986 period and increased to 0.24 mg/kg by 1992, and after 1992, the average mirex concentration decreased to 0.08 mg/kg in 1999. Comparison of percent lipid content from 1986 to 1999 found no significant changes (ANOVA, $F = 0.099$, df = 3,70, $P = 0.96$).

Within any given sampling year, mirex concentration was a function of weight (Figure 2, also ref *23*). If mirex availability to salmon were the same over time, a similar relationship of concentration versus weight should exist over the 22-year study period. That is, average mirex concentration would be a function of average weight of fish analyzed. This was true to some extent, as the highest average mirex concentration observed was for a year that had the second highest average fish weight (1992). However, the year with the highest average fish weight, 1999, had the lowest average mirex concentration (Table 2). Clearly, other factors were influencing mirex concentration. Fish weight should be taken into account in trend analysis rather than just employing simple averages of toxic concentration over time.

TABLE 2. Descriptive Statistical Data for Salmon Fillets Collected from 1977 to 1999 and ANOVA Results[a]

							ANOVA results	
year	1977	1982	1986	1992	1996	1999	*F*	*p*
Mirex (mg/kg)	0.22	0.18	0.19	0.24	0.16	0.08	7.325	<0.001
no. of samples	24	24	24	12	19	19		
SE	0.02	0.02	0.02	0.04	0.02	0.01		
range	(0.07−0.41)	(0.03−0.35)	(0.02−0.41)	(0.09−0.48)	(0.06−0.29)	(0.021−0.26)		
Tukey test p	0.000	0.003	0.001	0.000	0.043	*		
mean % lipid	NA	NA	3.36	3.88	3.62	3.81	0.9601	0.099
SE			0.427	0.555	0.326	1.276		
range			(0.35−9.05)	(1.9−7.9)	(1.4−6.37)	(0.52−17.28)		
weight (kg)	3.20	3.69	4.46	7.12	5.62	7.23		
SE	0.47	0.52	0.66	1.11	1.12	0.67		
length (cm)	62.19	64.15	70.13	82.56	69.10	80.00		
SE	3.41	3.15	3.67	5.32	5.23	2.96		
LSMEANS	0.27	0.22	0.20	0.18	0.15	0.07		
P/M ratio	0.3−0.4	0.60	0.42	0.43	0.38	0.37		

[a] Mirex concentrations are in mg/kg-wet weight. Percent lipid data are not available for 1977 and 1982 sampling years. SE = standard error. LSMEANS are the weight adjusted mirex concentrations (mg/kg) for each sampling year from the ANCOVA, and ratios of 8-photomirex to mirex (P/M) are presented. NA denotes data that is not available.

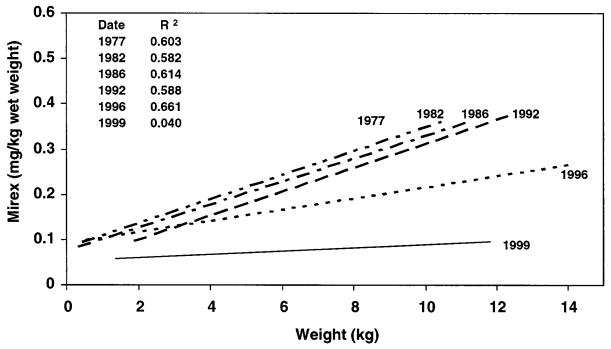

FIGURE 3. Relationship between mirex concentration and weight in Chinook and Coho salmon over a 22-year period. Lines represent simple regression lines.

To account for the differences in average fish weight between each collection year, the temporal trends in mirex concentration in salmon were evaluated by considering the slope of the regression line of mirex concentration versus fish weight for each collection year using ANCOVA with weight as the covariate (Figure 3). Pairwise *t*-test comparisons of the slopes of the ANCOVA regression lines for each collection year indicated that the slope of the 1999 regression line was significantly different (df = 1,5, $P \leq 0.014$, in Table 3) from the slopes of the regression lines from all previous years (1977, 1982, 1986, and 1992) except 1996 (df = 1,5, $P = 0.966$). Slopes for the 1977, 1982, 1986, 1992, and 1996 ANCOVA regression lines were not significantly different (df = 1,5, $P \geq 0.077$, Table 3). The slopes for the 1996 and 1999 regression lines were flatter (Figure 3), indicating that the mirex concentrations in the larger fish were decreasing. In 1999, mirex concentrations in salmon weighing 1.0−12 kg were below the United States FDA guideline for human consumption of 0.1 mg/kg for mirex (*1*), whereas only salmon weighing less than 2 kg were below this guideline in previous years (Figure 3). Interestingly by 1999, the regression line of mirex concentration versus fish weight was not significantly different from zero ($F = 1.22$, df = 1,17, $R^2 = 0.07$, $P = 0.21$), in contrast to all previous years in this study (Figure 3).

Utilizing the least-squares means (LSMEANS) of the weight adjusted mirex concentrations from the ANCOVA analysis, we compared the difference in the elevations of each regression line (Table 4). The weight adjusted mean mirex concentrations decreased from 0.273 in 1977 to 0.067 in 1999. A Tukey test (Table 4) revealed that the elevation of the 1977 regression line was significantly higher than that of all other years ($P \leq 0.005$) and that the elevation of the 1999 regression line was significantly lower than that of all other years ($P < 0.001$). Elevations of LSMEANS of 1982, 1986, and 1992 were not significantly different ($P \geq 0.129$), while the elevation for the 1996 regression line was significantly lower ($P \leq 0.008$) than those of 1977, 1982, and 1986 but not significantly different from ($P = 0.306$) 1992. The elevations of the weight versus mirex concentration regression lines seems to have been decreasing over time, which suggests

TABLE 3. ANCOVA Table and Slopes of the Regression Lines for Respective Years for the Relationship between Fish Weight and Mirex Concentration (ANCOVA)[a]

ANCOVA table	df	*F*	*p*
year	5	1.400	0.230
weight	1	130.414	0.000
year* weight	5	5.305	0.000

	pairwise comparison					
	1977 (*n* = 24)	1982 (*n* = 24)	1986 (*n* = 24)	1992 (*n* = 12)	1996 (*n* = 19)	1999 (*n* = 19)
	0.029[b]	0.027[b]	0.026[b]	0.027[b]	0.012[b]	0.004[b]
1977		3.120	3.738	3.780	0.080	0.014
1982			2.535	0.978	0.104	0.014
1986				1.730	0.077	0.014
1992					0.099	0.014
1996						0.966
1999						

[a] Also, *p* values of pair-wise comparisons of the slopes of the regression line for each year are included with a Bonferroni Layering Correction. Probability values < 0.05 indicate a significant difference. [b] Slope.

TABLE 4. Probability Values from a Comparison (Tukey Test) of Interyear Elevations of Regression Lines from 1977 to 1999 Utilizing LSMEANs of ANCOVA for the Relationship between Fish Weight and Mirex Concentration[a]

	1977	1982	1986	1992	1996	1999
1977		0.005	0.000	0.000	0.000	0.000
1982			0.501	0.129	0.002	0.000
1986				0.296	0.008	0.000
1992					0.306	0.000
1996						0.000
1999						

[a] General linear model in SPSS version 10.0 (SPSS Inc.).

that the mirex concentrations per kilogram of fish has been decreasing over time. There have been significant decreases in the regression line elevations on two different occasions. The first decline occurred between 1977 and 1982, after the use of mirex as a pesticide was banned in the United States and Canada. The second major decline occurred between 1996 and 1999; the cause of this decline is not well understood.

Discussion

Halfon (*30*) suggested that it would take 200−600 years before mirex-contaminated sediments were completely covered by mirex free sediments. Scrudato and DelPrete (*31*) agreed with this estimate based on the sedimentation rates of Kemp and Harper (*32*) and sediment concentrations near the Oswego River and Niagara River anomalies (*4*, *31*). Since mirex is one of the most stable compounds ever discharged into Lake Ontario (*33*) and because the nearshore bottom sediments redistribute into the water column (*31*), the predicted residence time and availability to biota was believed to be long. Biota associated with the contaminated sediment and important in the food web, such as *Mysis* and *Diporeia*, could continue to deliver mirex into the food web for many years, perhaps hundreds of years (*34*−*36*). However, results presented here suggest that either this is not happening or it is not a significant problem. Within 24 years of mirex being banned, mirex LSMEANS concentrations in salmon fillets have decreased significantly (ANCOVA, $P \leq 0.001$). In 1999, most salmonines below the weight of 12 kg were below the 0.1 mg/kg FDA action level for mirex, whereas 17−20 years ago only juvenile salmon were below that level and from 13 to 3 years ago only fish smaller than 2 kg had concentrations below the action level (Figures 2 and 3). Similarly, there is a general consensus that PCB concentrations in Lake Ontario lake trout decreased greatly between the 1970s and the 1990s (*37*−*39*).

Interestingly, the model of Flint and Stevens (*40*) that considered mirex loss through the food web, subsequent sedimentation, sediment burial, removal of mirex by the harvest of fish, and loss from outlets of the St. Lawrence River predicted an elimination of mirex from the Lake Ontario water column by 2010. This model appears to be more consistent with our findings than the Halfon (*30*) model. The major difference between the Halfon (*30*) model and the Flint and Stevens (*40*) model is that Flint and Stevens assumed that there were no new sources of mirex in Lake Ontario, whereas Halfon (*30*) assumed that contaminated sediments from the Oswego and Niagara rivers would be resuspended into the water column and deliver mirex to the food web for many years.

The question becomes what is the cause of the significant reduction in the LSMEAN mirex concentration in salmonine fillets? The proximal cause has to be a reduction within the levels of the trophic web, while ultimately, there should be a reduction in available mirex within the water itself. Hydrophobic contaminants, such as mirex, are readily removed from the water by adsorption to particulates, such as phytoplankton (e.g., ref *41*). It follows that a reduction in lake productivity, with an accompanying reduction in the amount of matter being produced at each trophic level, should lead to a reduction in the amount of mirex concentrations in the biota because theoretically, less organic matter and lipids are available to organisms per unit time. In Lake Ontario, the Phosphorus Abatement Program is responsible for successfully reducing the loadings of phosphorus to Lake Ontario. As a result of this reduction, ambient levels of phosphorus have decreased, causing phytoplankton abundances to decrease and water clarity to increase (*42*). Thus an overall decrease in lake productivity may be responsible for the declining trends of mirex contamination in salmon. As the biomass of organisms low on the food chain decrease (*42*), there should be less mirex available to organisms at the next trophic level, resulting in a decrease in mirex at each trophic level.

TABLE 5. Average Mirex Concentrations in Lake Ontario Biota over Time[a]

	1976 (*60*)	1986 (*40*)	1992 (*61*)	2000
alewife	0.19	0.13	0.034	0.010
yellow perch	0.08 (*1*)	0.055	ND	0.001
zooplankton	ND	0.0035	<0.001	0.0002

[a] Concentrations are in mg/kg wet weight, and ND represents no data available. References are listed in parentheses.

Indeed there is evidence of a decrease in mirex concentrations in various portions of the food web since the late 1970s. Mirex in alewife, a major food item of salmonines in Lake Ontario (*43*, *44*), has decreased considerably from 1976 to 2000 (Table 5). Major reductions have also been noted in yellow perch and zooplankton (Table 5). The average reductions in mirex concentrations are more than 10-fold at each trophic level from 1977 to 2000 suggesting that there is less mirex available for biomagnification. However, much of the decrease in phosphorus and phytoplankton abundances occurred in the early and mid 1980s (*42*) coincident with the small progressive, but not significant, decreases in mirex concentration from 1977 to 1992 (Figure 3) and not with the large significant mirex decrease in salmon tissue in the mid to late 1990s.

Certainly, the introduction of the zebra mussel (*Dreissena polymorpha*) and the quagga mussel (*Dreissena bugensis*) in Lake Ontario in the late 1980s may have also contributed to water clarity and removal of mirex from the pelagic food web. Zebra mussels have incredible filtering capacities and therefore could potentially accumulate high levels of contamination from the water or particle-bound contaminants such as mirex. Ultimately, mirex could be removed from the water column (water, particulate matter, and phytoplankton) to the benthic region by the accumulation of mirex in zebra mussel tissue. We have estimated the total mass of mirex bound up in zebra mussel tissue in Lake Ontario for 1991−1992 (25.7 kg) and 1995 (2.8 kg) based on mean zebra mussel abundance data from Haynes et al. (*45*). These estimations are liberal, as the entire surface area of the lake was used to determine entire lake abundance for zebra mussels. The 25.7 kg of mirex in zebra mussels in 1991−1992 is comparable to the 28 kg of mirex reported in fish in 1981 (*7*). However, the amount of mirex in zebra mussel tissue appears to be is trivial compared to the amount of mirex removed from the system by sedimentation (a total of 2000 kg).

Models have demonstrated that a forage base with younger less contaminated alewife or even less contaminated fish in general will result in a decrease in the pesticide concentrations in top predators (*44*, *46*−*49*). The declining forage base of alewife in Lake Ontario (*50*) could also result in reduced mirex concentrations in salmon. These models have also suggested, but not demonstrated, another pathway of reduction in salmonine mirex concentration, termed "growth dilution". These models predict contaminant concentrations in salmonines based on fish growth, amount of contaminants in the prey, amount of contaminants egested or excreted, respiration rates, and specific dynamic action (metabolic costs). In these simulations, when the intake and excretion of pesticide remained constant, piscivore growth increased, while piscivore contaminant concentration decreased in response to an increased growth rate or standing stock of forage fish (*46*). In Lake Ontario, where the alewife forage base was actually decreasing from 1977 to 1992 (*50*), it is unlikely that "growth dilution" is the cause of mirex reduction in salmon.

Another probable cause of mirex reduction in salmon is the recent reduction in alewife size. Salmon are size selective predators that attack larger alewives first. These large alewives are old, have been exposed to mirex longer, and have higher levels of contamination (*46*, *44*). It is possible that there are fewer large, highly contaminated alewives left in Lake Ontario because alewife abundance has been low in the recent years (prior to 2000), and the salmon have been readily removing these large fish over time. Temporal studies of salmon diet suggest that the number of alewives consumed has increased more than 3-fold from 1980 to 1993, but the average size and the mean weight of alewife in salmon stomachs have decreased at least 50% during that period (*47*). A reduction in the size in alewives in salmon stomachs suggests that alewife sizes in general have decreased over time (presumably due to the size selective predation behavior of the salmon), and recently the younger, less contaminated alewives make up a major portion of the salmon diet. We have found that alewife mirex concentrations have been declining over the years (Table 5), which may be due in part to the fact that alewife abundance is low in the lake and alewives are not living as long and picking up as much mirex before salmon prey upon them.

Ultimately, reductions in the mirex contamination of the food web must be due to a decrease in the mass of mirex in the water. Several potential pathways exist by which mirex mass in the water column is potentially reduced. These include photodegradation, volatilization into the atmosphere, sinking of organic particles containing mirex to the sediments, sport harvesting (i.e., fishing), and loss through the outlet of Lake Ontario at the St. Lawrence River.

Within the first few meters of the surface of a lake where ultraviolet light can penetrate, mirex can be chemically broken down into degradation products through different dechlorination processes (*8*). For example, when mirex in the water is exposed to ultraviolet light (*3*, *51*), photomirex or 8-monohydromirex is a degradation product. High ratios of P/M (photomirex/mirex) in organisms would indicate that mirex is being broken down into photomirex in the water and biomagnified through the food web (*52*). Since weather patterns have not changed significantly over the 22 years of the study, there is no reason to believe that the rate of conversion from mirex to photomirex would have changed. Only the availability of mirex may have changed. Further, there is no reason to believe that biological uptake of the two compounds would have changed over time. The relatively constant ratio of photomirex to mirex over the study period (Table 2) is only an indication of the relatively constant transformation of mirex to photomirex in the surface waters and suggest that the decrease in mirex concentrations in salmon are not a result of photodegradation.

Unlike the relatively high amounts of PCBs lost by degassing from Lake Michigan (*53*), the volatilization of mirex into the atmosphere is minimal (*54*). Although mirex has a low volatility from water and a high solubility in biological tissue, mirex can volatilize from a lake and be carried by the wind to land systems (*53*). However, atmospheric transport is unlikely to effectively reduce concentrations in Lake Ontario due to a low Henry coefficient, $H = 7 \times 10^{-4}$ (*55*). Also, because mirex is more hydrophobic than for example PCBs, mirex is associated with dissolved organic matter and particles and less available for vaporization. Furthermore, summer epilimnetic temperatures have not changed, so there is no basis for an increase in rate of volatilization of mirex from Lake Ontario. Major losses of mirex to the atmosphere are not likely (*54*).

Besides volatilization and photodegradation, other potential pathways of mirex loss from the water column include transport by organisms into the terrestrial or stream habitats (*56*, *57*), sinkage of mirex-laden organisms to the sediments, sport fishing, and loss through the St. Lawrence River (*40*). Although demonstrated, the movement of mirex by salmonine migration into stream habitats and by aquatic insects feeding on salmonine carcasses is minimal (*56*, *57*), while mass removal by harvested sport fish is not likely (L. Skinner, personal communication). The loss via the St. Lawrence River is inferred to be a significant loss mechanism based on modeling and by the sheer volume of water that moves through the system from Lake Ontario. However, loss via the St. Lawrence River as well as sedimentation of dead organisms would suggest a relatively constant rate of mirex loss over time, which is not what was observed (Figure 3).

Perhaps the greater rate of reduction in mirex in salmon tissue observed in the mid to late 1990s is due to reduced loading of mirex from the watershed into Lake Ontario, rather than mirex losses from the water column. At the former Hooker Chemical Company Niagara Falls site, the original source of mirex in Lake Ontario, a slurry wall has been installed (1993−1994) around the entire plant including the landfill area, a bedrock and overburden groundwater collection and treatment system was installed (1996), and a former sewer line carrying nonaqueous phase liquids (including mirex) to the Niagara River was plugged, cleaned, and converted to part of the collection and treatment system (*58*). Additionally at the Hyde Park Landfill, the landfill was enclosed and encapsulated and now has water collection and treatment systems, all similar to the Hooker Chemical site. Two years of monitoring data has shown that chemical concentrations in the off-site bedrock groundwater have decreased (*58*). In 2000, as a component of the binational four party agreement to reduce toxics in Lake Ontario, the Ontario Ministry of Environment conducted biomonitoring in the drainways from the sites using clams and have demonstrated significant declines in mirex concentrations although it is still present in small concentrations (L. Skinner, personal communication).

In summary, 24 years after mirex was banned as a pesticide in Canada and the United States, mirex LSMEANS concentrations in Lake Ontario salmon fillets have decreased significantly. Since salmon are a wide-ranging, pelagic species in Lake Ontario (*59*) feeding on actively schooling alewives, analytical results are likely to be representative of the entire lake. The observed reductions in mirex in salmon appear to be fairly accurately predicted by the simulations of Flint and Stevens (*40*), which suggested reductions and the elimination of mirex from the system by 2010 with sedimentation and loss of mirex through the St. Lawrence River as the primary mechanisms of loss from the system. However, the greater rate of reduction of mirex in salmon tissue in the mid to late 1990s argues against this as the only pathways of reduction. Instead the control and removal of contaminated groundwater at the former Hooker Chemical site initiated in 1993 is coincident with the larger reductions in mirex in salmon tissue observed in the mid to late 1990s. In actuality, all three mechanisms are likely contributing but at differing rates and time scales. Because short-term changes in fish tissue residues may represent departures due to factors other than ecosystem changes in concentration, such as general fish health, the short term decline observed between 1996 and 1999 should be viewed with caution. Only further trend analysis will confirm the recent greater temporal rate of decrease in mirex concentration in salmon tissue. Current health advisories for consumption of salmonines from Lake Ontario should be reexamined with a sampling design encompassing a larger spatial area.

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